

## Stratospheric ClO profiles from McMurdo Station, Antarctica, spring 1992

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**Abstract.** We describe ground-based measurements of ClO made at McMurdo Station, Antarctica, during September and October 1992. Vertical profiles were retrieved from molecular rotational emission spectra at 278 GHz. Peak mixing ratios of  $1.6 \pm 0.3$  ppbv were seen in mid-September at approximately 18 km altitude, suggestive of somewhat larger quantities than were measured at the same site and season in 1987. As the core of the polar vortex moved away from McMurdo by early October, the ClO mixing ratio at this altitude dropped to less than 0.2 ppbv, coincident with increasing temperature, ozone, and NO<sub>2</sub>. The diurnal variation of ClO was also observed. The lower stratospheric layer from 15 to 27 km was found to reach approximately midday abundance by 2–3 hours after sunrise. The column abundance in this layer began to decrease by the period 4–2 hours before sunset and had declined to approximately one quarter of its midday value by 2–0 hours before sunset. In contrast, the ClO column in the upper stratosphere, from 28 to 50 km, built up slowly until midday and remained large while sunlight persisted.

### Introduction

After the discovery of the seasonal ozone hole over Antarctica [Farman *et al.*, 1985], the first verification of chlorine as the causal agent was made in September 1986 and again in 1987 at McMurdo Station (77.8°S, 166.7°E) using ground-based millimeter wave spectroscopy to identify and quantitatively measure a telltale layer of ClO [de Zafra *et al.*, 1987, 1989], coincident with the altitude region of severe ozone depletion [Hofmann *et al.*, 1989]. The same relationship was observed by in situ ER-2 aircraft measurements of the lower half of the anomalous ClO layer in 1987 [Brune *et al.*, 1989; Anderson *et al.*, 1991] and large-area studies are now possible with MLS (Microwave Limb Sounder) millimeter wave data from UARS [Waters *et al.*, 1993]. The mechanisms resulting in the formation of the Antarctic ozone hole are now fairly well understood [e.g. Solomon, 1990]. During the polar winter, heterogeneous reactions on polar stratospheric cloud (PSC) particles convert chlorine from inactive forms (ClONO<sub>2</sub>, HCl) to active forms (Cl<sub>2</sub>, HOCl), which are rapidly photolyzed

in early spring. The ozone-depleting catalytic cycle which is of primary importance at low altitudes proceeds through the formation and subsequent photolysis of the ClO dimer [Molina and Molina, 1987]. Freed chlorine then reacts with ozone and forms ClO in the lower stratosphere. The precondition for the development of the ozone hole is denitrification of the polar vortex, caused by conversion of NO<sub>x</sub> to HNO<sub>3</sub> in solution on PSCs or sulfate aerosols. This greatly reduces or prevents the deactivation of chlorine through reaction with NO<sub>2</sub> to form chlorine nitrate (ClONO<sub>2</sub>) in the region 15–25 km where PSCs typically form. We present here new measurements of stratospheric ClO taken in 1992 and compare these measurements with our previous data.

### Instrumentation and Data Processing

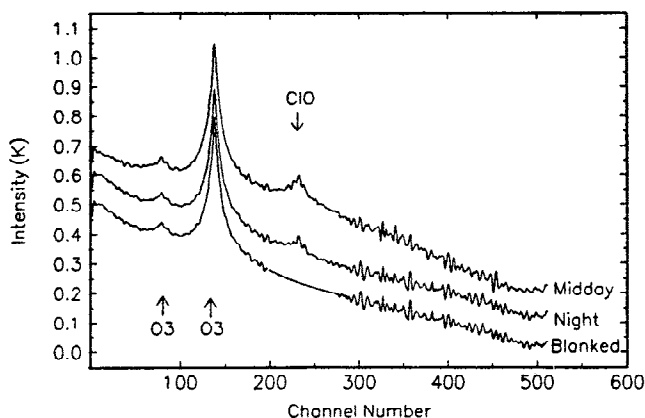
Our data were taken with a ground-based millimeter wave receiver/spectrometer similar in its operating mode to that described by Parrish *et al.* [1988]. We began a new series of yearly observations at McMurdo in 1992 with an improved version of this millimeter wave receiver, employing a superconducting (SIS) tunnel junction heterodyne mixer for higher sensitivity [de Zafra *et al.*, 1994]. The resulting decrease in the noise temperature (increased sensitivity) through use of the SIS receiver has made it possible to achieve greater temporal resolution than before. For most of the measurements described here a filter bank spectrometer, with a band pass of 512 MHz and 1-MHz resolution, was used, although for one short interval we employed an acousto-optical spectrometer (AOS) with 600-MHz band pass and 2-MHz resolution.

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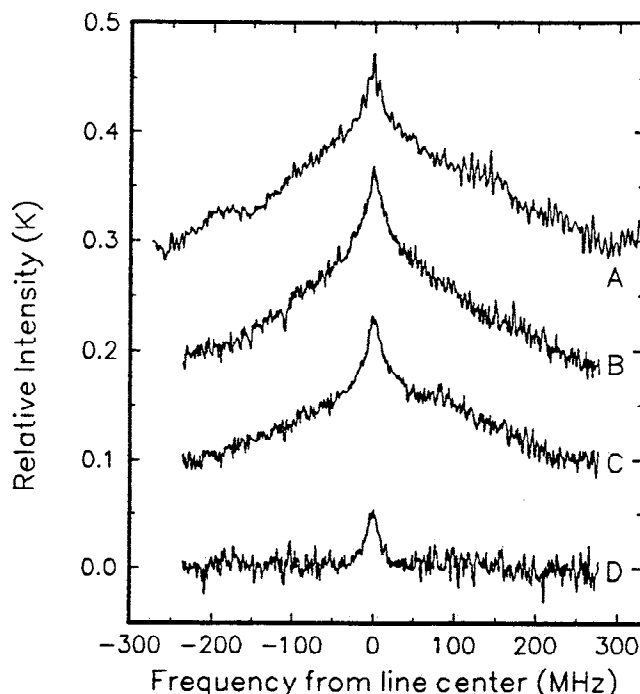
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We measure the pressure-broadened emission spectrum of ClO at 278.631 GHz ( $\lambda \approx 1.1$  mm). There are two significant ozone emission lines in our spectral band pass. Since ClO has a strong diurnal variation, while ozone tends to be fairly constant over a given 12- to 24-hour period, these can be rather accurately removed by subtracting nighttime spectra from daytime spectra. The nighttime spectrum used for subtraction is weighted, whenever possible, toward data as far after sunset as possible. Because the layer of ClO at 35–40 km shows a relatively slow decay throughout the night, a spectral region  $\pm 40$  MHz around line center is blanked, and a second-order polynomial is extrapolated from the adjacent 50 channels over this section of the spectrum. The day-minus-night subtractions also remove most instrumental baseline features present in the spectra, when they remain essentially constant between day and night spectra. This processing is illustrated graphically in Figure 1, and the results of day-minus-night subtraction are shown in Figure 2.

This paper addresses two different features of the low altitude ClO layer during the austral spring of 1992 – its diurnal change and its longer-term change. To study the latter during the evolution of the ozone hole, the midday data were analyzed, where midday is defined to be from 4 hours after sunrise to 4 hours before sunset at 18 km. Data were taken around the clock, weather permitting. Previous measurements of ClO [de Zafra *et al.*, 1987, 1989] have shown that ClO in the lower antarctic stratosphere increases quite rapidly after sunrise and decreases quickly near sunset, so that this definition of “midday” is fairly conservative. We have di-



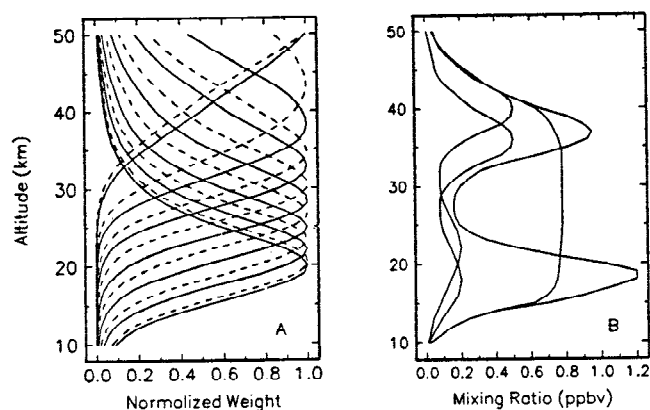
**Figure 1.** Typical midday, night (predawn), and blanked spectra (night with emission from high altitude layer of ClO blanked and replaced with a second-order fitted curve between channels 196 and 276). The broad midday emission spans the entire spectral window and is obtained, along with an increased high altitude daytime component (see Figure 2) by subtracting “blanked” from “midday” spectra. Channel width is 1.176 MHz/channel. The ClO emission is centered at 278,633 MHz. Strong and weak ozone lines are visible at channels 138 and 79, respectively. The increased noise rightward of channel 300 is due to electronic interference which does not affect the line shape.



**Figure 2.** ClO spectra of midday averages from McMurdo, 1992: (a) September 15, (b) September 19–20, (c) September 22–23, and (d) October 2–4. Midday includes data from 4 hours after sunrise to 4 hours before sunset at 18 km. The data of September 15 were taken using an acousto-optical spectrometer, which has a slightly larger band pass than the filter banks used for all other data. Spectra are offset by 0.1 K from one another for clarity.

vided our data into four representative periods in the austral spring of 1992, based on a reasonable quality of data and representation of different periods during evolution of the ozone hole: September 15, 19–20, and 22–23 and October 2–4. The midday-averaged pressure broadened emission line spectra from these four periods are shown in Figure 2. Here, spectral intensity has been normalized to that which would be observed in the zenith direction in the absence of tropospheric attenuation, following the methods given by Parrish *et al.* [1988] to compensate for geometrical path length in the actual observing direction, receiver sensitivity, and time-varying tropospheric attenuation.

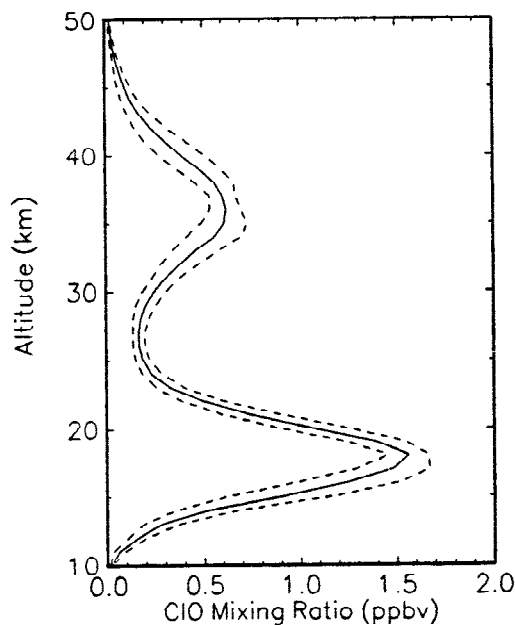
To obtain vertical profiles for ClO, each of the spectra in Figure 2 was deconvolved using pressure and temperature profiles determined from local meteorological or ozonesonde balloon records for the appropriate dates. Deconvolutions were carried out using the Twomey-modified Chahine inversion method [Chahine, 1970; Twomey *et al.*, 1977]. To reduce the bias introduced by the initial conditions, inversions were run with the four different starting profiles and the two different sets of weighting functions shown in Figure 3, giving a total of eight trial recoveries from each spectrum. The consistency of the resulting deconvolutions can be seen from the example in Figure 4, which shows the mean



**Figure 3.** (a): The two sets of weighting functions used for the Chahine-Twomey deconvolution of pressure-broadened spectra. (b): the four starting profiles used to initialize the retrieval algorithm. The two larger profiles are based on ER-2 data [Brune *et al.*, 1989; Anderson *et al.*, 1991] from 13–16 km. Vertical profiles discussed in this article are averages of deconvolutions employing the eight permutations of weighting functions and starting profiles.

and one standard deviation of the eight retrievals for the September 19–20 data.

The 512-MHz limit of spectral band pass causes the lowest weighting functions to have rapidly decreasing influence below roughly 16 km. We allow the inversion algorithm to vary the initial profile from 12 km upward to create a smooth transition, but below ~16 km the influence of the initializing profiles is increasingly dominant. To establish a reasonable lower profile, the



**Figure 4.** The mean (solid line) and standard deviation (dashed lines) of the eight retrievals for midday, September 19–20, 1992, using the eight permutations of the weighting functions and starting profiles in Figure 3.

two larger of the four initializing profiles shown in Figure 3 are based on an average of ER 2 measurements for the Antarctic vortex of 1987 in the 13- to 16-km region [Brune *et al.*, 1989], using the corrected values given by Anderson *et al.* [1991].

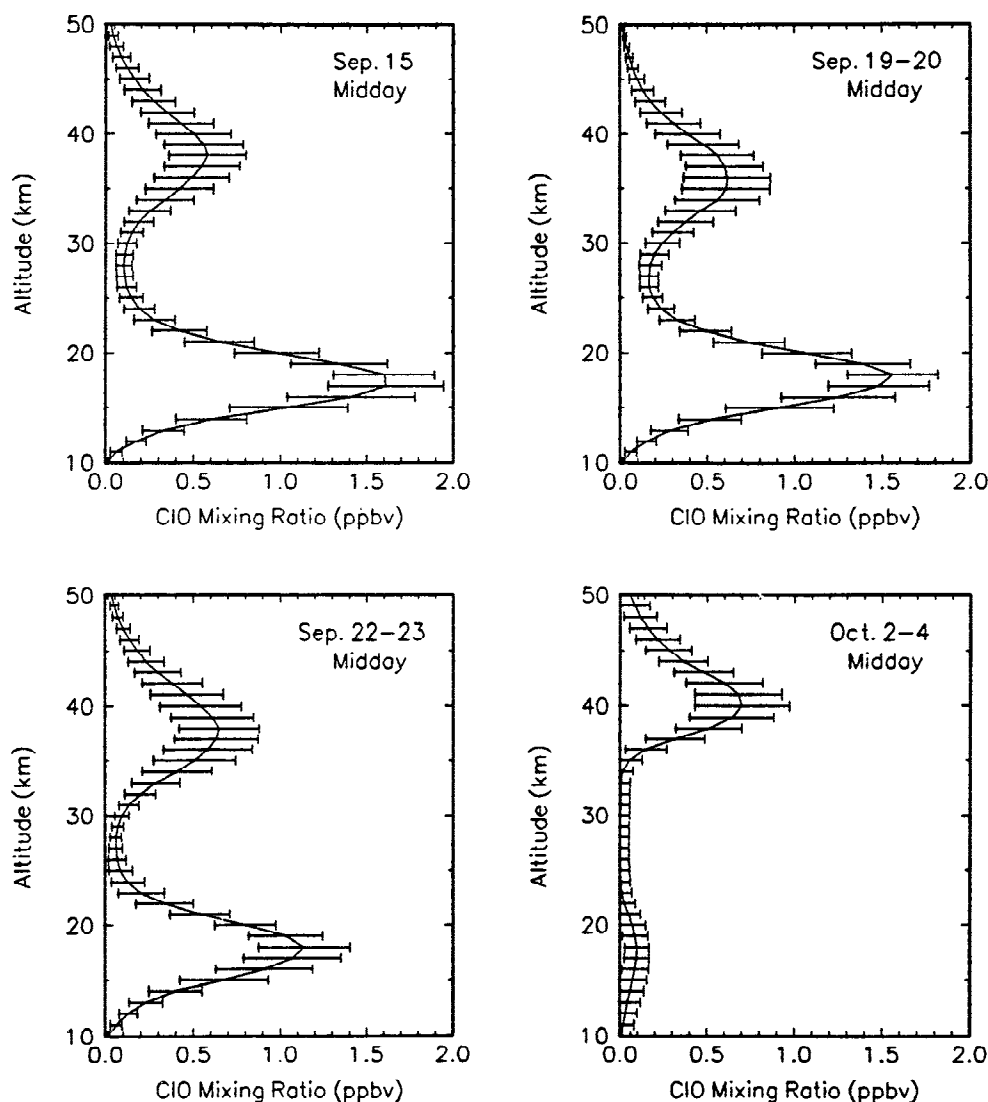
## Results

### Longer-Term Change

The average of the eight retrievals for each of the four data periods analyzed is shown in Figure 5. The error bars shown here represent the standard deviation of the total uncertainty, including uncertainties in calibration of the receiver sensitivity as well as in profile retrieval. A full discussion of uncertainties in profile retrieval, including height resolution, is outside the scope of this paper but is given by in Emmons and de Zafra [1994], Emmons [1994], and Shindell *et al.* [1994]. The lower-altitude layer actually represents the difference between midday and nighttime mixing ratios, since only the narrow, high-altitude spectral contribution can be effectively “blanked out” of the subtracted nighttime spectrum. However, model results for conditions appropriate to the Antarctic spring vortex [e.g., Crutzen *et al.*, 1992] indicate that nighttime CIO concentrations within the ozone hole are less than 0.1 ppbv at approximately 20 km. Table 1 gives the total column densities derived from the retrieved CIO midday profiles. The uncertainties given in the table represent the standard deviation of the eight deconvolutions discussed above, plus a 12% calibration uncertainty.

The primary changes in CIO during September–October, evident in the vertical profiles shown in Figure 5, are the slight decrease in CIO at low altitudes from September 19–20 to September 22–23, followed by a dramatic decrease between September 22–23 and October 2–4. The former change cannot be related to a shift in the position of the vortex, and is not likely to be a result of early renitrification (*see, for example, Crutzen et al.* [1992]). The moderate differences in observed CIO in late September are likely simply the result of inhomogeneity within the polar vortex. The latter change, the dramatic decrease between September 22–23 and October 2–4, can be attributed to a dynamical source, based on the position of the polar vortex and coincident measurements of temperature, ozone, and  $\text{NO}_2$ .

A useful guide to the position and boundaries of the vortex is provided by maps of Ertel’s potential vorticity (EPV). From analyses of National Meteorological Center (NMC) data provided by NASA Goddard Space Flight Center, it is evident that McMurdo was inside the vortex when data was collected in September and then in the edge of the vortex during October 2–4, coinciding with the dramatically decreased lower layer of CIO which we observed during this period. The vortex “edge” is defined here to mean the midrange in the steepest gradient in EPV contours, approximately a value of  $-4 \times 10^{-5} \text{ K m}^{-2} \text{ kg s}^{-1}$  on the potential temperature surface  $\theta = 475 \text{ K}$ .



**Figure 5.** Retrieved profiles for midday ClO at McMurdo Station, Antarctica, 1992, for the data shown in Figure 2. Error bars indicate one standard deviation of the total retrieval uncertainty (including calibration, atmospheric parameter uncertainties, and retrieval algorithm limits).

Maps of total column ozone as measured by the Total Ozone Mapping Spectrometer (TOMS) on METEOR 3, obtained from the NASA Goddard Space Flight Center database, show that the region of ozone depletion was within the polar vortex boundary as defined above and

**Table 1.** Column Densities for Midday ClO Data From Derived Profiles

Date	Column, $\times 10^{15}$	15–27 km, $\times 10^{15}$	28–50 km, $\times 10^{13}$
Sept. 15	$2.1 \pm 0.2$	$2.1 \pm 0.2$	$6.0 \pm 0.6$
Sept. 19–20	$2.0 \pm 0.2$	$1.9 \pm 0.2$	$7.1 \pm 0.7$
Sept. 22–23	$1.5 \pm 0.2$	$1.4 \pm 0.2$	$6.1 \pm 0.6$
Oct. 2–4	$0.16 \pm 0.02$	$0.12 \pm 0.02$	$3.9 \pm 0.2$

Densities are in molecules per square centimeter and are given for total column (15–50 km) and for the upper and lower layers separately. See text for discussion of listed uncertainties.

that a steep gradient in ozone was colocated with the gradient in potential vorticity. For each of the four periods analyzed here, most of the vortex core (as delineated in the EPV maps) was below 175 or 150 Dobson units (DU). During mid to late September, the ozone column above McMurdo ranged from approximately 250 DU to 175 DU. In early October, however, McMurdo was under the steep ozone gradient at the vortex boundary and the column was 300–325 DU despite the continued low values in the vortex core. A significant fraction of this increased amount of ozone arose from the influx of large ozone mixing ratios above 20 km, as shown by ozonesonde balloon flights over McMurdo [Johnson *et al.*, 1994]. This was accompanied by a dramatic increase in temperature above 20 km.

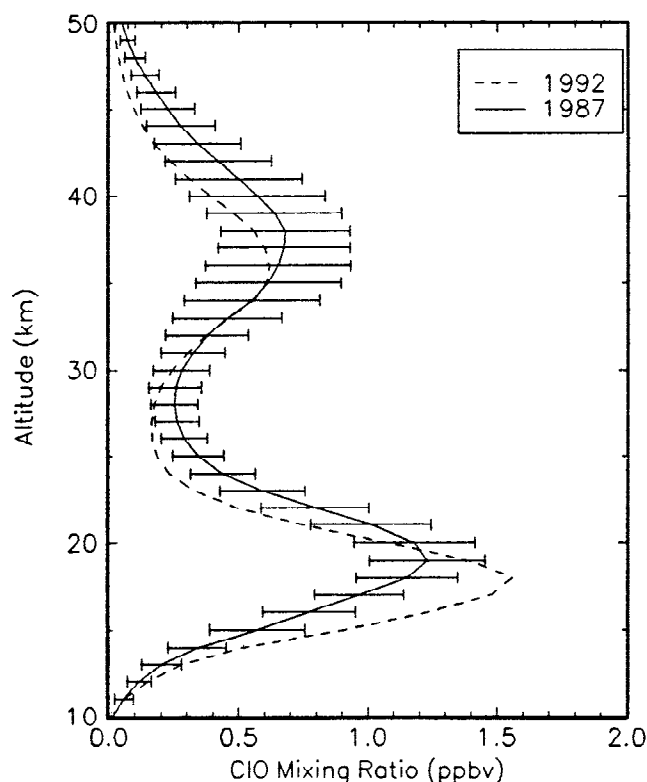
A comparable pattern was seen in ground-based UV spectroscopy measurements of NO<sub>2</sub> at McMurdo (S. Solomon, personal communication, 1992). Large varia-

tions in the total column of  $\text{NO}_2$  were seen as the position of the vortex changed, with concentrations lower when McMurdo was closer to the center of the vortex in mid-September and larger as the vortex edge moved over by the end of the month, coinciding with the drop in ClO mixing ratios.

We conclude that comparison of our ClO measurements with all of the other coincident data indicates that the observed change in midday ClO occurring between mid to late September and early October was primarily due to dynamics: the maps of EPV, along with the balloon measurements of temperature and ozone, show that the vortex edge moved over McMurdo by early October, bringing air with a higher concentration of  $\text{NO}_2$ , and consequently less ClO. A high-pressure system lying south of New Zealand caused this strong displacement of the vortex and persisted through October 9, when our observations ended. We were thus unable to sample vortex air for ClO content in October 1992 and cannot determine from our data when renoxification of the lower stratosphere may have begun.

### Comparison With 1987 Data

A vertical profile was retrieved from the midday-minus-night spectrum of data taken by us during September 20–24, 1987 [de Zafra *et al.*, 1989], using the same combinations of weighting functions and starting profiles as were used for the results above. Figure 6 shows



**Figure 6.** McMurdo ClO mixing ratio profiles for September 20–24, 1987, and September 19–20, 1992. Error bars on the 1987 profile are one standard deviation total uncertainties as in Figure 5.

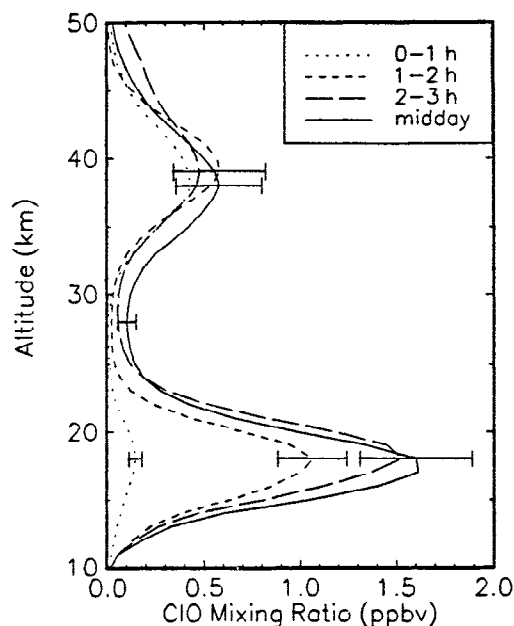
the retrieved profile, with uncertainties calculated as for the 1992 midday profiles, compared with the profile for September 19–20, 1992. Potential vorticity maps indicate that the vortex was positioned similarly over McMurdo during these two periods. Conditions within the vortex were also quite similar in 1987 and 1992.

The amount of chlorine being produced in the troposphere is increasing approximately 3% a year [World Meteorological Organization, 1991], and the added influence of heterogeneous processing on Pinatubo aerosols was a contributing factor to denoxification of the stratosphere in 1992. Comparison of our profiles for 1987 and 1992 as shown in Figure 6 suggests a corresponding increase in polar stratospheric ClO; however the difference between the two profiles is not statistically significant. Furthermore, a comparison of the September 20–24, 1987, profile with the September 22–23, 1992, profile would show almost no difference. The maximum concentration of the lower ClO layer is ultimately limited by the amount of free chlorine available but is also modulated by temperature, which determines the rate of ClO dimer formation and dissociation, and by transport and other physical factors. Temperature and ozone profiles measured by balloon from McMurdo in 1987 [Hofmann *et al.*, 1989] indicate that the vortex during this period had slightly lower temperatures than in 1992 but very similar ozone amounts between 16 and 25 km, suggesting that the average ClO content was similar (Note that the efficiency of the ClO dimer cycle in freeing chlorine, and thus in destroying ozone, is quadratically dependent on the concentration of ClO.) The primary effect of Pinatubo aerosols in 1992 may have been to enhance ozone depletion at lower altitudes (12–16 km) [e.g., Johnson *et al.*, 1994]; however, our measurements are quite insensitive to increased ClO in that region as a result of the large pressure broadening in relation to the available spectral bandwidth (see weighting functions in Figure 3).

Since the upper layer of ClO ( $\approx 38$  km peak) should be minimally affected by denitrification and since dimer formation is negligible in that region, it is likely that an increase of total chlorine in the stratosphere would be evident there. The high altitude profiles for 1992 and 1987 do not differ in a statistically significant way in Figure 6. The larger uncertainty in profile retrievals at high altitudes, however, makes it impossible for us to conclude from these data whether or not there has been an increase in ClO abundances in the upper stratosphere.

### Diurnal Variation

The data from the morning of September 15, 1992, have an unusually good signal to noise ratio due to very good observing conditions. We have therefore been able to divide this single day's data into 1-hour bins up to midday to examine the rate of increase in ClO after sunrise. After midday we have continued an analysis of the diurnal change using data grouped into 2-hour segments, due to somewhat worsening observing conditions. Figure 7 shows the retrieved profiles for sunrise



**Figure 7.** Retrieved profiles from September 15 for the first three 1-hour time blocks after sunrise and the 4.5-hour midday block. Representative error bars are standard deviation of the total uncertainty as in Figure 5.

through midday. It is evident that the amount of low-altitude CIO increases rapidly after sunrise and by 2–3 hours later is already near its maximum value. The rapid growth of the low-altitude layer after sunrise is primarily due to the photolysis of the CIO dimer into free chlorine, which then reacts rapidly with ozone to form CIO.

The column densities for each time block are given in Table 2, where the midday bin has now been divided into two bins of 3 hours each for greater time resolution. As in Table 1, the uncertainties are derived from the standard deviation of the eight retrievals used in the data

**Table 2.** Column Densities for Diurnal Variation on September 15

Bin, hours*	Column, $\times 10^{15}$	15–27 km, $\times 10^{15}$	28–50 km, $\times 10^{13}$
0–1	$0.21 \pm 0.02$	$0.18 \pm 0.02$	$3.3 \pm 0.3$
1–2	$1.3 \pm 0.1$	$1.2 \pm 0.1$	$3.8 \pm 0.4$
2–3	$1.8 \pm 0.1$	$1.8 \pm 0.1$	$4.3 \pm 0.7$
3–6	$2.0 \pm 0.1$	$2.0 \pm 0.1$	$5.6 \pm 0.6$
7–4	$2.2 \pm 0.2$	$2.2 \pm 0.2$	$6.3 \pm 0.5$
4–2	$1.5 \pm 0.2$	$1.5 \pm 0.2$	$7.2 \pm 0.9$
2–0	$0.64 \pm 0.06$	$.56 \pm 0.05$	$7.9 \pm 1.3$
0–2	$0.22 \pm 0.12$	$.18 \pm 0.09$	$5.6 \pm 0.9$

Densities are in molecules per square centimeter and are given for total column (15–50 km) and for the lower and upper layers separately. See text for discussion of listed uncertainties.

\* The first four bin times are given with respect to sunrise (at 18 km); the last five are with respect to sunset. Sunset at 38 km occurs almost 40 min later, so that for the upper layer, the 0–2 hours after sunset bin actually includes a large fraction of data from before sunset.

deconvolution, plus a 12% calibration uncertainty. We note that sunrise and sunset times at 18-km altitude were used in defining the time bins.

The column abundance of CIO in the lower stratosphere increases rapidly, as was seen in the vertical profiles shown in Figure 7. A clear maximum is seen around midday, extending from the period 2–3 hours after sunrise to 7–4 hours before sunset. The column abundance begins to decline during the period 4–2 hours before sunset, drops to slightly more than one quarter of the midday maximum by 2–0 hours before sunset, and has reached roughly one tenth of the maximum by 0–2 hours after sunset.

In contrast, the column abundance of CIO in the upper stratosphere increases slowly until midday, which occurs near the beginning of the 7–4 hours before sunset bin. The abundance remains large and seems to even increase, though the increase is within the large uncertainty in the late afternoon data, through the remainder of the sunlit portion of the day, including the period 2–0 hours before sunset. A decrease in the column abundance is evident in the period 0–2 hours after sunset, though sunset at 38 km occurs nearly 40 min later than sunset at 18 km, so that this bin actually includes a significant fraction of data from before sunset in the upper stratosphere.

Our results indicate a slower daily buildup of the CIO column in the upper stratosphere than that which occurs in the midlatitude model of *Ko and Sze* [1984]. The daytime buildup of CIO in the region 28–50 km, where the CIO dimer concentration is negligible, is primarily due to the conversion of chlorine from  $\text{ClONO}_2$  and  $\text{HOCl}$  throughout the day.

## Summary

We have presented vertical profiles of CIO derived from new ground-based measurements made at McMurdo Station, Antarctica, during the austral spring of 1992. Enhanced mixing ratios of  $1.6 \pm 0.3$  ppbv were seen in mid-September at approximately 18 km, somewhat larger than quantities measured at the same site and season in 1987. A dramatic decrease in the CIO mixing ratio in this altitude range, to less than 0.2 ppbv, was observed in early October. This change was coincident with increasing temperature, ozone, and  $\text{NO}_2$  as the polar vortex moved away from McMurdo. In addition, we have recovered vertical profiles showing the diurnal variation of the lower stratospheric CIO layer in mid-September and give the changes in column density associated with this cycle throughout the stratosphere. The CIO mixing ratio in the lower stratosphere was found to reach approximately its maximum midday value by 2–3 hours after sunrise. The column amount in this lower layer had decreased to approximately one quarter of the midday maximum by the period 2–0 hours before sunset. In the upper stratosphere, however, the column abundance of CIO built up slowly until midday and remained large throughout the duration of solar exposure.

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